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Modified Carbon Nanotubes for Improvement of Biosensor Electrodes

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***Abstract*—Electrical conductive and water dispersive carbon nanotubes were firstly prepared by admicellar polymerization for using to improve biosensor electrodes. Copolymer of polyaniline (PANi) and polyvinyl acetate (PVAc) was synthesized as a nanofilm coated on the surface of carbon nanotubes (CNTs). FT-IR was used to characterize the copolymer film coated on the surface of CNTs. SEM and TEM were also used for morphology observation of the admicellar-modified CNTs on the surface. Lastly glassy carbon electrode samples prepared from the modified CNTs were fabricated for testing the sensibility of the electrode by cyclic voltammetry (CV). The results showed that the modified CNTs by PANi-co-PVAc coating were successfully prepared. From cyclic voltammetry test of ascorbic acid (AA) analysis, the results were found that the biosensor electrodes using the PANi-co-PVAc modified CNTs provided higher sensitivity for measuring AA at low concentration. This work could imply that adding the PANi-co-PVAc modified CNTs in biosensor electrodes have the potential for application in biosensor.**

***Index Terms*—Modified carbon nanotubes, admicellar polymerization, surface modification, biosensor electrodes.**

I. INTRODUCTION

Carbon nanotubes (CNTs) are the well-known nanomaterials with excellent properties of mechanical, electrical, thermal and magnetic properties due to the high aspect ratio of nanoscale. Normally CNTs are nondestructive in water and tend to aggregate from interface interaction or van der Waals force [1]. However most applications of CNTs need good water dispersion. To enhance the water dispersive property of CNTs, many researchers have developed their surface to be hydrophilic. Functionalization is a chemically modified surface technique of materials that can be divided into covalent and non-covalent bonding [2]-[4]. Covalent functionalization is the technique for modifying material surface with the covalent bond between the material surfaces with molecules of added chemicals. The examples of covalent functionalization for improving water dispersive CNTs include oxidation reaction with concentrated nitric acid and sulfuric acid [5]-[7] and polymer grafting of poly(acrylamide) [8]. Non-covalent functionalization is a non-destructive modification of material surface with only interaction of the material surface and the added chemical with some of hydrogen bonding or polar-polar interaction or hydrophobic-hydrophobic interaction. Non-covalent functionalization for improving water dispersion of CNTs includes surfactant adsorption on material surface [9], polymer wrapping with polyvinyl pyrrolidone and polystyrene sulfonate [10] and biopolymer wrapping with chitosan [11]. Almost reviewed literatures to modify the surface of CNTs for water dispersion improvement used covalent functionalization. The advantage of non-covalent functionalization based mainly on physical adsorption of surfactant or polymer is less destructive to the structure and surface of CNTs than covalent functionalization [12]-[14].

Admicellar polymerization is classified as a non-covalent functionalization involving the ultrathin film of polymer formed in the bilayer surfactant adsorption on the material surface. The surfactant bilayer adsorbed on the material surface is so called “admicelle”. The synthesized polymer used is for either hydrophilic or hydrophobic surface modification of any materials. The process of this technique consists mainly four steps: admicelle formation, adsolubilization, in-situ polymerization and surfactant removal. Admicellar polymerization was first introduced by Wu et al in 1987 [15]. However admicellar polymerization was utilized to modify different materials with various polymers for a wide range of applications, such as polystyrene coated on cotton [17], polymethyl methacrylate coated on CNTs [18] and aluminum pigments [19], polystyrene coated precipitated silica [20] and improving antimicrobial polymer coated on nanoclay [21]. For improving the hydrophilicity of materials by polymer coating, PAA and PVAc were used to modify sand particle surface [22]. All former examples were the research for improving hydrophobic surface. Importantly for application in biosensor electrodes, CNTs must well disperse in water and still maintain the electricity. In this study, PANi and PVAc copolymer (PANi-co-PVAc) was considered to synthesize on the surface of CNTs according to electrical conductive polymer and water-soluble polymer of PANi and PVAc, respectively.

Vitamin C or ascorbic acid (AA) is one of the most vitamin needed to measure the concentration in various biochemical plant such free radical scavenging, cancer preventing and improving immunity. Conventionally the determinations of AA are based on enzymatic methods, titration methods, HPLC analysis and UV-Vis detection. Recently biosensor has been interested for electrochemical detection, basically oxidized of AA. However direct oxidation of AA requires high potential of electrode for its oxidation products with

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poor reproductivity, low selectivity and sensitivity. To develop electrode, CNTs were interested to devote. Many researchers modified CNTs to increase their dispersion for good stability for electrode fabrication and biochemical measurement. CNTs were discovered as good electrode materials by Iijima [23] since 1991. Then it has been used as modified glassy carbon electrodes [24], [25]. The PANi-co-PVAc modified CNTs were considered to improve the water dispersion and electrical conductivity added in the biosensor electrode for measuring low concentration of AA.

II. EXPERIMENTAL

A. Materials

Carbon nanotubes (CNTs), average size of 27 nm diameter and 10 µm length, were purchased from Nano Generation (Thailand). Sodium dodecyl sulfate (SDS) was purchased from Merck (German). Two monomers, aniline (ANi) and vinyl acetate (VAc), were purchased from Sigma Aldrich (USA) and Sigma Aldrich (Germany), respectively. Amonium persulsate (APS) was purchased from Ajax Finechem (Australia). All chemicals were used as received.

B. Admicellar Polymerization

CNTs were chemically modified by admicellar polymerization. Surface modification of this technique was followed with its four main steps. First admicelle formation step was carried out by adding 1g CNTs in 50 mL vessel of 5,000 µM SDS solution and continuously stirred for 24 h at room temperature. Second the monomer (ANi or VAc or both) at the surfactant:monomer molar ratio of 1:10 and APS (as an initiator) based on mole of monomer with 1:1 were added into the solution. The mixture was continuously stirred for 24 h at room temperature for adsolubilization step. Then the third step, polymerization was carried out by heating up the mixture system to 90 ℃ and continuously stirred for 2 h. Lastly, the modified CNTs were taken out and washed with the distilled water several times to remove the outer layer of the adsorbed SDS surfactant. The modified CNTs were then dried in an oven at 60 ℃ for 24 h.

C. Characterizations

Fourier-Transformed Infrared Spectroscopes (FT-IR) from Perkin Elmer, Spectrum 2000 using attenuated total reference (ATR) was the appropriate technique for carbon nanotube characterization and used for this work.

Scanning Electron Microscopy (SEM) from JEOL, JSM-5410LV, was used to observe the morphology of the CNT surface. The samples of unmodified and modified CNTs were analyzed at 200 × magnifications. The samples were prepared by pasting on brass grids and then placed in the sputter coater under vacuum for gold coating.

The morphology of unmodified and modified CNTs was also confirmedly by Transmission Electron Microscopy (TEM) from JEOL, AJEM-200CX. The samples were photographed at 200 nm scales with 100000 × magnifications. Samples were prepared by sonication in ethanol. After that the mixtures were dropped on formvar carbon grids. They were left over night before analysis.

D. Electrochemical Measurement

Cyclic voltammetric and amperometric measurements were performed. Three electrodes composed of a platinum counter electrode, a silver-silver chloride (Ag/AgCl) reference electrode and a glassy carbon working electrode that fabricated using bare CNTs and modified CNTs. Software NOVA 1.7 was used to control electrical potential and to measure electrical current.

Ascorbic acid (AA), or known as vitamin C, was elected to use for electrochemical detection. The electrolyte was the mixture solution of 200 mM AA in 0.5 M KCl.

III. RESULTS AND DISCUSSION

A. FT-IR Characterization

The FT-IR spectra of unmodified or bare CNTs and three modified CNTs are shown in Fig 1.

The spectra of the CNTs coated with PNAi homopolymer, PVAc homopolymer and PNAi-co-PVAc copolymer were clearly different from bare CNTs. The functional groups of PNAi and PVAc were significantly shown to confirm the success preparation of PNAi-modified, PVAc-modified and PNAi-co-PVAc-modifide CNTs.

For bare CNTs in Fig. 1(a), there is no band on the spectrum as shown for the functional group of PNAi and PVAc. The peaks of the spectra of the all modified CNTs were very small due to very thin film of polymer coating on the surface of CNTs. PNAi-coated CNTs in Fig. 1(b) displays the peaks of amine group (N-H) at 3654 - 3758 cm^{-1} to confirm nanofilm of PNAi coated on the modified CNTs. Fig. 1(c) displays the peak of PVAc spectra at 1727 cm^{-1} of the stretching vibration of carboxyl group (C=O), 1357 cm^{-1} of the methyl ester group ($CH_3(C{=}O)$), and 1414 cm^{-1} of the hydroxyl group (C-O) thus confirming the existence of PVAc nanofilm appeared on the surface of CNTs. The FT-IR spectra of both PNAi and PVAc were presented in Fig. 1(d) to confirm PNAi-co-PVAc copolymer nanofilm covered on the CNTs.

B. Morphology Study by SEM Micrographs

Fig. 2 shows the SEM images 200 × magnifications of nanoparticles of bare CNTs, PNAi-modified CNTs, PVAc-modified CNTs and PANi-co-PVAc modified CNTs. Fig. 2(a) shows the aggregate of bigger bare CNTs, whereas the modified CNTs with PAA (Fig 2b), with PVAc (Fig 2c) and with PANi-co-PVAc (Fig 2d) were smaller due to no aggregation. The reason was that the ultrathin film of polymer coated on the surface of CNTs reduced the van der Waals interaction between nanotube-nanotube interfaces. The SEM images also showed the changed morphology between the bare CNTs and modified CNTs. The surface of modified CNTs in Fig 2b, 2c and 2d shows clearly smoother surface without any attached small particles when compared with bare CNTs in Fig 2a.

C. TEM Images

TEM images at 100000 × magnifications in Fig. 3 show the morphology for comparison between bare CNTs and modified CNTs. The bare CNTs (Fig 3a) looks like the fibers without any coating on the surface, whereas the PANi-coated CNTs (Fig. 3b), PVAc-coated CNTs (Fig. 3c) and PANi-co-PVAc modified CNTs (Fig. 3d) explicitly show ultrathin film formed on the modified fibers. The TEM images clearly confirmed that the coated polymer film synthesized on the surface of CNTs by admicellar polymerization technique was a nanofilm with good dispersion around the CNT fiber surface.

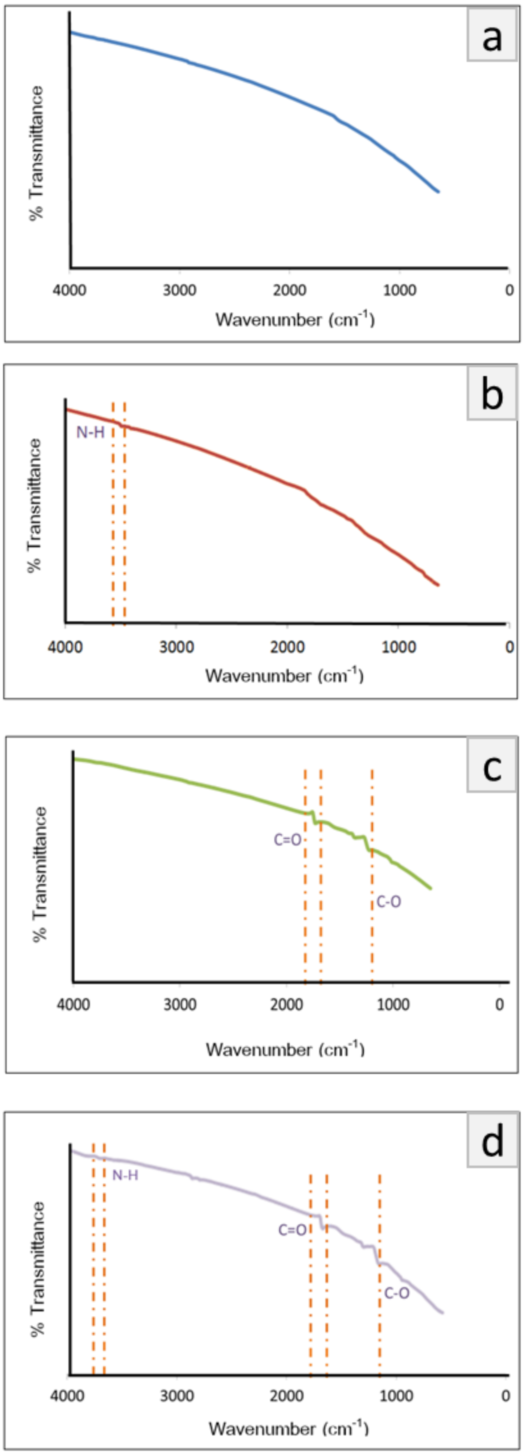


Fig. 1. FT-IR spectra of (a) unmodified CNTs, (b) PANi-modified CNTs, (c) PVAc-modified CNTs and (d) PANi-co-PVAc modified CNTs.

D. *Electrochemical Test*

The electrochemical test of biosensor electrodes was obtained by measuring AA low concentration. The cyclic voltammogram of glassy carbon electrodes adding bare CNTs and modified CNTs was examined as the results Fig. 4. The results show two cycles, representing red line for 0.5 M KCl reduction/oxidation curves and dashed blue line for 0.5 M KCl with 200 mM AA reduction/oxidation curves of each substrate. The electrodes of four substrates prepared by adding bare CNTs, PANi-coated CNTs, PVAc-coated CNTs and PANi-co-PVAc modified CNTs were used to observe cyclic voltammogram as Fig. 4(a), 4(b), 4(c) and 4(d), respectively. Ag/AgCl electrodes were used as the referent electrodes.

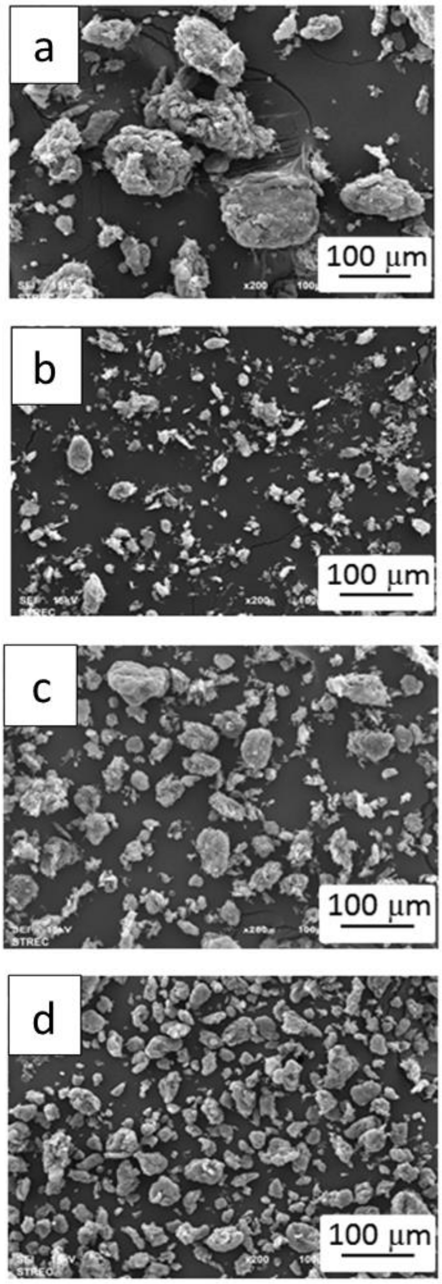


Fig. 2. SEM micrographs of (a) unmodified CNT, (b) PANi-modified CNT, (c) PVAc-modified CNT and (d) PANi-co-PVAc modified CNT.

The results showed that the CV curves of the electrodes prepared by PVAc-coated CNTs (Fig. 4c) and the electrodes prepared by PVAc-coated CNTs (Fig. 4d) presented the specific electrical signal of AA reduction, the flat line of the under curve of the red line. The reason is that PVAc is the polar substrate to capture AA molecules. Thus the electrode adding PVAc-coated CNTs or PANi-co-PVAc modified CNTs could improve the sensibility of AA measuring, but adding PANi-co-PVAc modified CNTs gave higher sensibility.

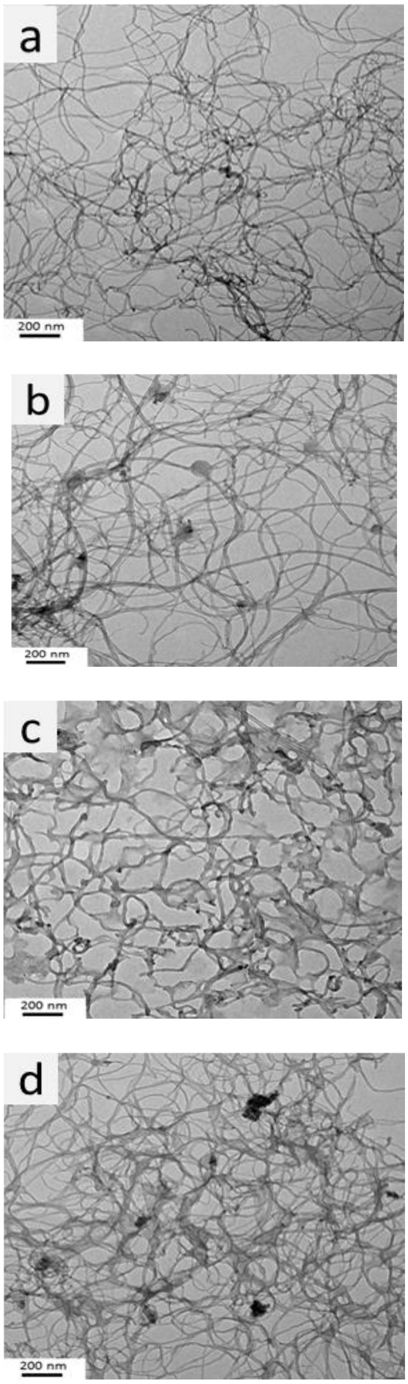
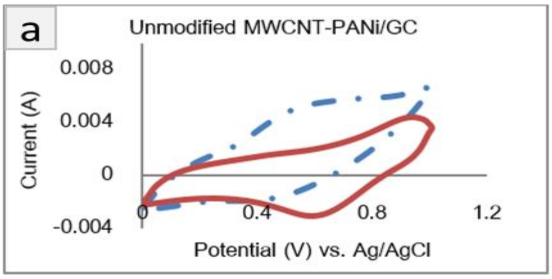


Fig. 3. SEM micrographs of (a) unmodified CNTs, (b) PANi-modified CNTs, (c) PVAc-modified CNTs and (d) PANi-co-PVAc modified CNTs.



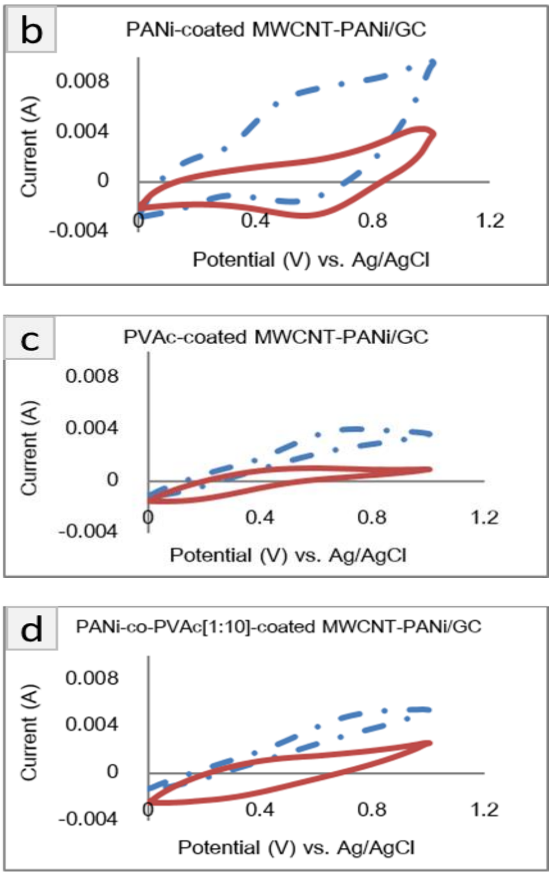


Fig. 4. Cyclic voltammogram of GC with different modified CNTs in 0.5 M KCl (red line) and in 200 mM AA and 0.5 M KCl (dashed blue line) of (a) unmodified CNT, (b) PANi-modified CNT, (c) PVAc-modified CNT and (d) PANi-co-PVAc modified CNT.

IV. CONCLUSION

The improvement of biosensor electrodes by adding the modified CNTs with copolymer of PANi/PVAc to the glassy carbon electrodes was successful for measuring AA test observed from cyclic voltammogram. The electrodes were fabricated by adding 10% modified carbon nanotubes of polyaniline dissolved in chloroform for the optimum application with high accuracy and sensibility for low AA concentration tested at 200 mM.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

We contributed all research and data analysis. We had also approved the final version.

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